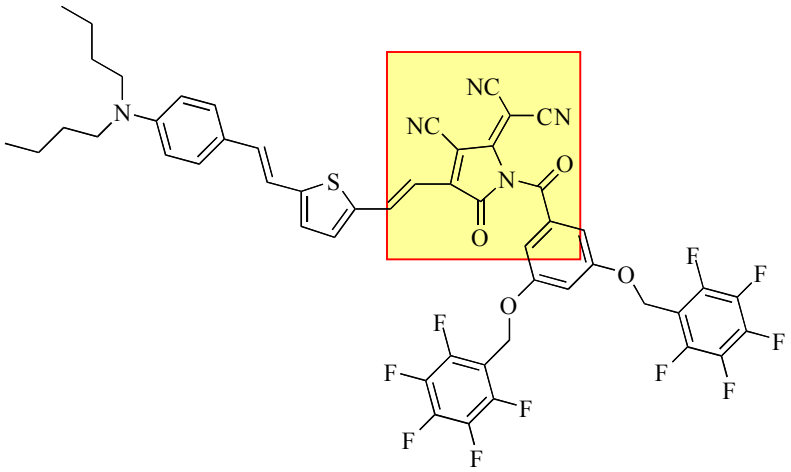
Development of Synthesis, Processing, and Characterization Techniques for Next Generation Electroactive Materials

Larry Dalton, University of Washington, DMR-0092380

Quantum mechanical (QM) calculations of molecular hyperpolarizability have been carried out for a number of chromophore structures. A tricyanopyrroline acceptor was predicted to exhibit twice the hyper-polarizability of the tricyanofuran acceptor (Science, 288, 119, 2000). This prediction has been experimentally confirmed by the HyperRayleigh Scattering measurements on model compounds and by electro-optic measurements (see accompanying figure). QM calculations also suggest other modifications that could result in electro-optic (EO) coefficients as high as 300 pm/V at telecommunication wavelengths. Statistical mechanical calculations suggest dendrimer and dendronized polymer structures that could result in additional



An electro-optic chromophore based on the tricyanopyrroline acceptor (see insert) yields 101 pm/V at 1.55 microns when incorporated into amorphous polycarbonate (20 wt %).

dramatic improvements in EO activity (J. Phys.: Condens. Mater., 15, 897, 2003). Organic EO materials have been used to fabricate active ring microresonators (J. Lightwave Technol., 20, 1968, 2002) suitable for active wavelength division multiplexing and other applications.

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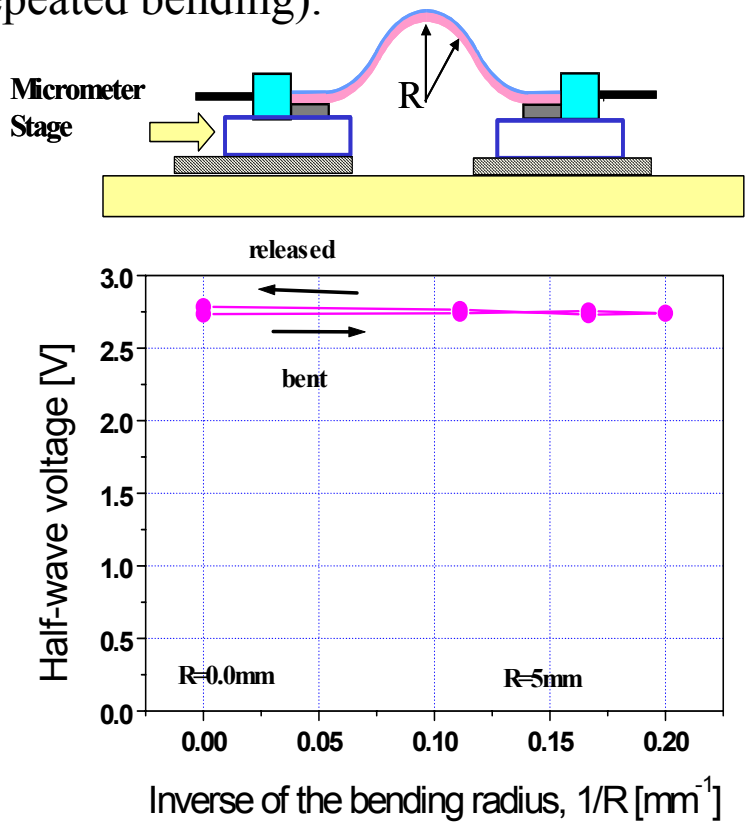
Conformal and flexible devices can be fabricated from organic EO materials (see below—no change in drive voltage with repeated bending).

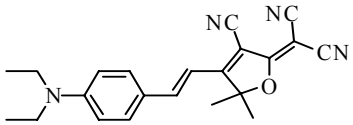


Technology Transfer: Materials have been transitioned to industry (Boeing, Lumera, etc.) and to DoD (Air Force and Navy Laboratories).

Education: Five graduate students, three undergraduate students, and two high school students have carried out research with NSF support. Professor Dalton organized and lectured in the ACS-PRF/NSF sponsored workshop on the "Chemistry of Information Technology Research" and lectured in the NASA REU Space Grant Program in the summer of 2003. The research results of this grant have been featured in community educational experiences including multiple UW Science Forum (televised), Seattle Technology Alliance, Seattle Community Development Roundtable, UW Fall Orientation, and high school outreach lectures. A collaborative research/education exchange has been established with Norfolk State University.

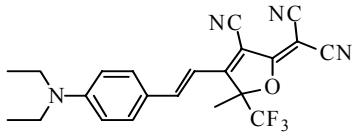
The ultimate objective of research in the 4th and 5th years of this grant is to develop a systematic approach to the preparation of nanostructured organic electroactive materials for the realization of dramatically enhanced electro-optic, electronic, magnetic, sensing, and photovoltaic properties. With organic electroactive materials the critical issue in the control of electrical, magnetic, and optical properties is the precise three-dimensional spatial control of π-electron orbitals. The relative separations and orientations of such orbitals must be controlled both intra and intermolecularly. Precise spatial control of orbitals is critical not only for properties such as electro-optic activity, electrical conductivity, etc. but also for chemical and photochemical stability. Indeed, properties such as hyperpolarizability, charge separation, and charge transport can be considered to represent various points on a continuum of charge perturbation by applied (and internal) fields. Like charge delocalization (or quasi-delocalization), spin delocalization will depend on the positioning of π-orbitals in an electroactive organic material. In our proposed research, we will use quantum and statistical mechanical calculations, building upon successes realized with the development of state-of-the-art organic electro-optic materials, to guide the systematic design of nanostructured organic material lattices yielding dramatically improved properties. We will then use nanostructural engineering based on use of dendrimers, dendronized polymers, and supramolecular bundles (e.g., mimics of discotic liquid crystals) to implement theoretically inspired material designs.

Recently, we have employed a combination of quantum mechanics and statistical mechanics to realize organic electro-optic materials exhibiting electro-optic coefficients of greater than 100 pm/V at telecommunication wavelengths (wavelengths centered about 1.3 and 1.55 microns). Our approach is illustrated by the following Figures.



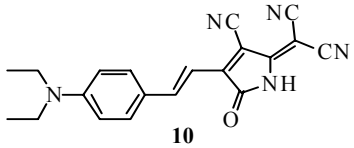
1

μ	= 11.8 D		
ß $_{o}$	= 23.8 x 10	$^{-30}$	esu
ß $_{1907\ nm}$	= 31.6 x 10	$^{-30}$	esu
μß $_{o}$	= 280.8 x 10	$^{-48}$	esu
μß $_{1907\ nm}$	= 372.9 x 10	$^{-48}$	esu
λ $_{max}$	= 390 nm		



2

μ	= 11.9 D		
ß $_{o}$	= 34.4 x 10	$^{-30}$	esu
ß $_{1907\ nm}$	= 46.6 x 10	$^{-30}$	esu
μß $_{o}$	= 409.4 x 10	$^{-48}$	esu
μß $_{1907\ nm}$	= 554.5 x 10	$^{-48}$	esu
λ $_{max}$	= 403 nm		

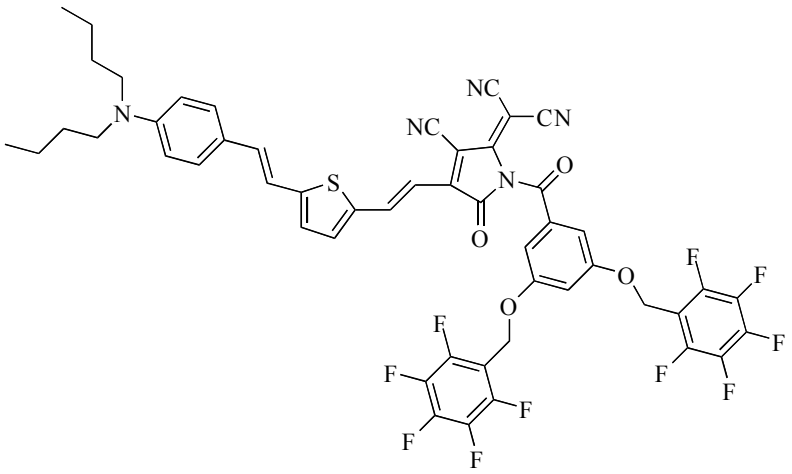


10

μ	= 11.7 D		
ß $_{o}$	= 43.0 x 10	$^{-30}$	esu
ß $_{1907\ nm}$	= 62.4 x 10	$^{-30}$	esu
μß $_{o}$	= 503.1 x 10	$^{-48}$	esu
μß $_{1907\ nm}$	= 730.1 x 10	$^{-48}$	esu
λ $_{max}$	= 430 nm		

Figure 1. Dipole moments (μ), hyperpolarizabilities (β), and absorption maximum (λ_{max}) calculated by semi-empirical methods for representative structure modifications. Predicted trends are confirmed by experimental measurements (e.g., HyperRayleigh Scattering, HRS).

In Fig. 1, we show the theoretically predicted variation of molecular hyperpolarizability associated with variation of the acceptor portion of an electro-optic chromophore. The first chromophore on the top left incorporates the tricyanofuran (TCF) of CLD and FTC chromophore structures used by our research group in 2000 to demonstrate organic electro-optic modulators exhibiting drive voltages of less than one volt [1,2]. Subsequently, our research group demonstrated that electro-optic activity could be significantly enhanced by replacing even one of the methyl groups of the TCF acceptor with a trifluoromethyl group [2]. This observation was also independently reported by researchers at Lockheed Martin and at Corning [2]. As shown in Fig. 1 top right, this trend is theoretically predicted by calculations based on model compounds. These model compounds have been synthesized and HRS measurements made yielding values consistent with theoretically predicted trends. In Fig. 1 bottom, a tricyanopyrroline (TCP) acceptor structures is predicted to yield even greater molecular first hyperpolarizability, which has been experimentally verified by HRS measurements on the model compounds. We have also synthesized the chromophore shown in Figure 2, which incorporates a TCP acceptor.Figure 2. A



chromophore incorporating a TCP acceptor moiety that when incorporated in 20 weight percent into amorphous polycarbonate (Aldrich) yields at electro-optic coefficient of 101 pm/V at 1.55 microns is shown.

Even for a relatively short chromophore π-electron structure, a value of 101 pm/V is obtained for the chromophore of Fig. 1. Theory further predicts that an additional factor of 2-3 enhancement in molecular hyperpolarizability will be obtained if the phenyl ring of the chromophore of Fig. 2 is replaced with a thiophene group and the thiophene moiety of Fig. 1 is replaced with a thiazole group—we refer to such structures as "gradient bridge" structures as the electron donating power of components decreases and the electron accepting power increases as one moves from left to right across the chromophore. Moreover, theory predicts that molecular hyperpolarizability can be improved using mixed ligand acceptors rather than acceptors based on three cyano ligands (2). Of course, theoretical calculations also suggest improvements to be realized in molecular hyperpolarizability using modified donor structures (2). Indeed, in the research effort proposed for years 4 and 5, we will implement theoretical suggestions already noted and conduct further calculations on promising structures. Theoretical calculations will also be extended to investigate the relationship of molecular structure to other electroactive properties including two photon absorption (and third order optical nonlinearity in general), unimolecular rectification, charge injection, etc. As will be noted later, charge injection and transport depends strongly on

intermolecular interactions and hence are best studied by calculations executed on supramolecular bundles.

The electroactive properties of organic materials will depend not only upon molecules such as chromophores but also upon intermolecular interactions, i.e., the three dimensional spatial arrangement of molecules. For example, electro-optic activity requires that molecules be organized in a noncentrosymmetric lattice of chromophores. In our 2000 *Science* paper (1), we demonstrated that both intermolecular electrostatic interactions involving π-electrons and steric (nuclear repulsive) interactions compete to define experimentally observed noncentrosymmetric order and hence electro-optic activity. In 2001, we demonstrated that the rotational restrictions associated with the covalent bonds used to incorporate multiple chromophores into a single dendrimer structure could be used to achieve improved noncentrosymmetric order and hence electro-optic activity (3). This concept has been extended to dendronized polymers as shown in Figure 3. Such materials have structures that can mimic the tobacco mosaic virus.

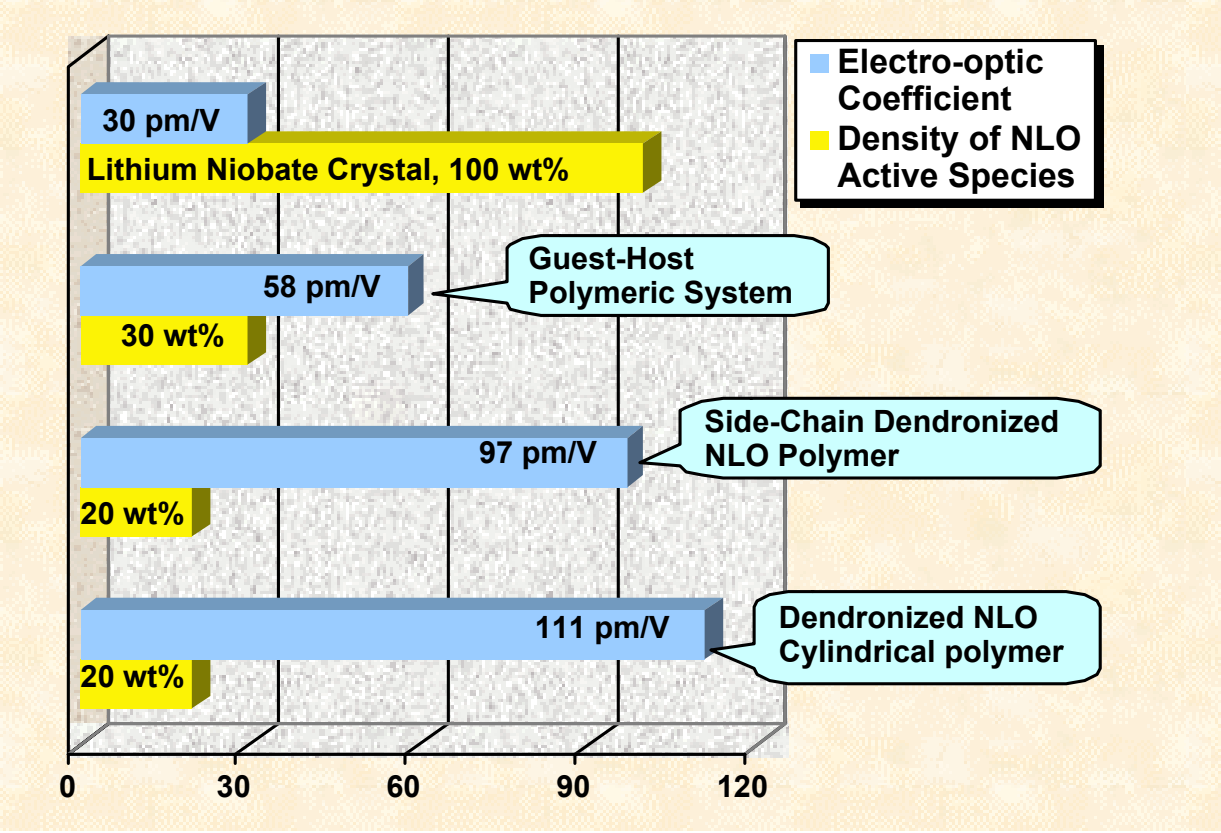


Figure 3. The electro-optic activity of the same chromophore (CLD of reference 1) in three types of lattices is shown (4). These include physical incorporation into a guest host lattice and into two types of dendronized polymer lattices. Lithium niobate is shown for comparison.

From consideration of Fig. 3, it is clear that a combination of steric effects and motional restriction associated with covalent bonds help oppose the tendency of intermolecular dipole-dipole interactions to drive centrosymmetric organization of chromophores. Electro-optic activity is effectively doubled by use of nanostructural control of the three dimensional spatial organization of chromophores. As is evident from our publications and NSF progress reports,

we have used statistical mechanical calculations, including pseudo-atomistic Monte Carlo calculations, to quantitative understand the role of various intermolecular (and intramolecular) forces in defining ultimate supramolecular order. Both analytical equations and numerical results have been produced and discussed (2) and have led to preparation of first generation multiple chromophore dendrimer (3) and dendronized polymers structures (4).

In the proposed research, we will continue the correlated theory/synthesis/nanostructural processing paradigm that has worked so well in leading to electro-optic activities on the order of 100 pm/V. During the next two years, we propose to achieve electro-optic coefficients on the order of 300 pm/V (an order of magnitude greater than the best inorganic material lithium niobate). From a consideration of the remarks of the preceding pages, it is clear that this is a very realistic if amazing goal (amazing in terms of technological impact because drive voltages on the order of a few tenths of a volt could be achieved with a wide variety of device configurations impacting telecommunications, computing, defense, and transportation). If a perfect noncentrosymmetric (ferroelectric) chromophore lattice could be produced, electro-optic coefficients of greater than 1000 pm/V would result. This would be a truly transformative technological achievement. Preliminary psuedo-atomistic Monte Carlo calculations suggest that this may be possible with bundled supramolecular building blocks shown in Figures 4 and 5.

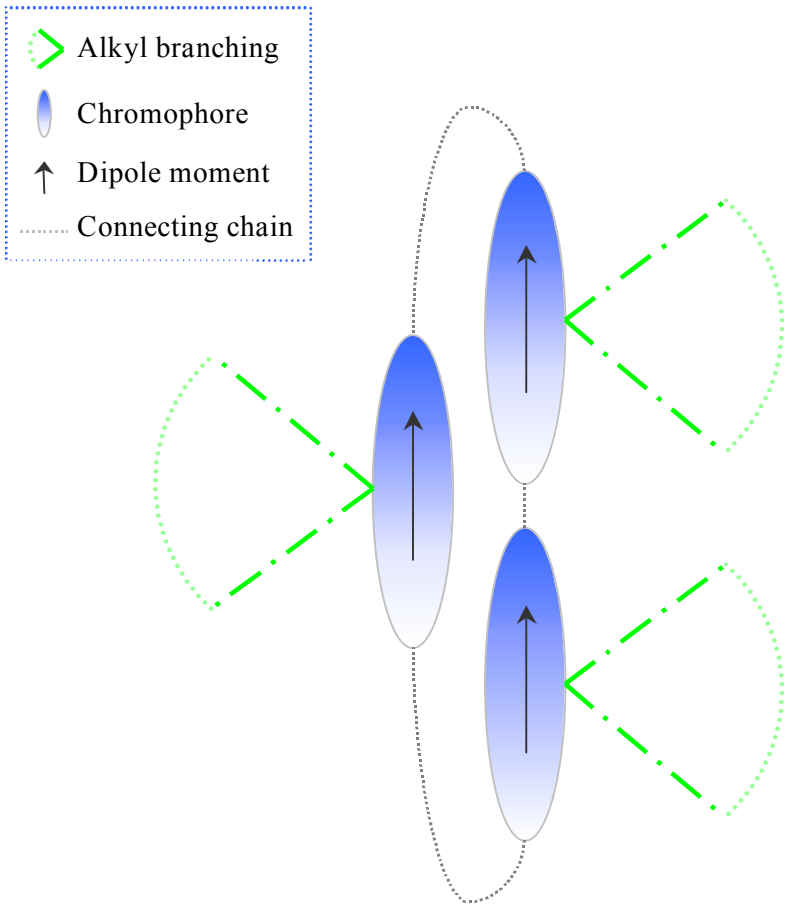


Figure 4. A "J-aggregate" like bundle of electro-optic chromophores is shown. Dendritic wedges led to an overall discotic-like shape. Dipole and hyperpolarizability tensors point in the same direction. The dendritic wedges oppose centrosymmetric ordering of the bundles.

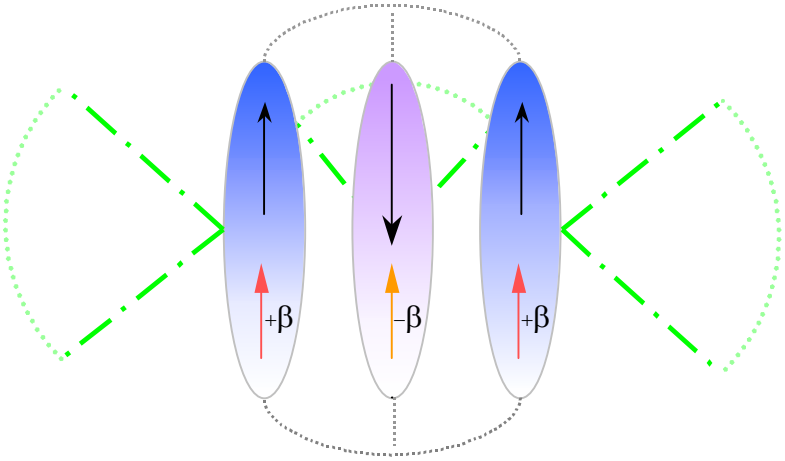


Figure 5. A discotic shaped chromophore bundle prepared from positive and negative β chromophores is shown. A two chromophore bundle can equally well be employed. This can be considered to be a "sacrificial dipole" structure in that centrosymmetric organized chromophores (in the bundle) are used to minimize unwanted intermolecular dipole-dipole interactions. The molecular hyperpolarizability tensors are additive in contrast to the dopole tensors.

Of course, the structures shown in the cartoons of Figs. 4 and 5 are highly oversimplified. Semi-empirical and density functional theory (DFT) calculations on such bundles suggest that the detailed structure of the bundles will be critical. For optimum electro-optic activity, one wants to avoid the π–π interactions between chromophores as such interactions act to reduce hyperpolarizability. We have demonstrated in our recent presentation at the Chicago American Chemical Society Meeting (2003) that such multi-chromophoric bundles can indeed be synthesized in an efficient manner. More recently, we have completed the synthesis of the first +β/−β chromophore bundle. This material, synthesized in tenths of a gram quantity is awaiting HRS and electro-optic measurements but has been analytically characterized by mass spectrometry, NMR, and elemental analysis as well as other standard molecular characterization measurements.

Preliminary electrical conductivity measurement suggests that high electrical conductivity is being observed potentially reflecting an acentric (e.g., ferroelectric) discotic stacking. Charge transport is undesirable for electro-optic materials (and would suggest the need for structural modification to effect better isolation of stacked disks) but suggests an approach to organic semiconductor and photovoltaic materials exhibiting charge mobilities comparable to silicon but compatible with solution processing.

In our proposed research, we will pursue both theoretical and experimental investigation of multi-chromophore containing bundles of controlled shape (e.g., discotic). This is clearly not a trivial undertaking either from a theoretical or experimental perspective; however, we believe that both the theoretical and synthetic tools are in hand to take on this intimidating challenge. The outcome, of course, could be complex ferroelectric and ferromagnetic (and related) structures by design. If successful, we believe that this approach could revolutionize organic nonlinear optics, organic electronics, and organic magnetics/spintronics. In one sense, this work is a logical extension of work being carried out by Michael Rubner (MIT), Tobin Marks (Northwestern), and our group; however, we believe that new theoretical and synthetic methods bring a dramatic enhancement to the effort. We believe that for the first time dipole-dipole, ionic, steric (nuclear repulsive and covalent bond restrictions), etc. interactions can be analyzed

and employed in a logical way control the precise organization of organic moieties in a surpramolecular framework (nanostructured lattice).

A side advantage of our approach to intermolecular/supramolecular engineering is that we can control auxiliary properties such as optical transparency (loss), thermal stability, photochemical stability, and mechanical properties. The approach can readily be extended to optimization of a wide range of physical properties beyond those mentioned above. We have already demonstrated sensor paints (5) based on nanostructured hybrid (organic/inorganic) dendrimer materials and improved organic light emitting device materials (6).

In years 4 and 5 of this grant, we will give increased attention to methods of processing materials including in addition to spin casting, we will consider layer by layer deposition techniques and vapor phase deposition techniques involving aerosol or electrospray approaches. In addition to reactive ion etching techniques for fabricating prototype device structures, we will pursue e-beam and soft lithography methods. Although the fundamental focus of the proposed research will be the development of new materials with dramatically improved properties, we believe that a strength of our research program has also been the development of improved processing techniques and the ability to demonstrate prototype devices. For example, we have demonstrated that organic nonlinear optical waveguide structures can be fabricated and integrated with semiconductor VLSI electronics and silica fibers (7), that complex three-dimensional active circuits can be fabricated from organic nonlinear optical materials (8), and that ring microresonator and photonic bandgap devices can be fabricated and that exceptional performance can be achieved for applications such as active wavelength division multiplexing (9). We have also demonstrated a putative advantage of organic materials that highly robust conformal and flexible devices based on thin film organic materials can be fabricated. In the following figures, we demonstrate that no degradation is performance is observed even for high degrees of bending.

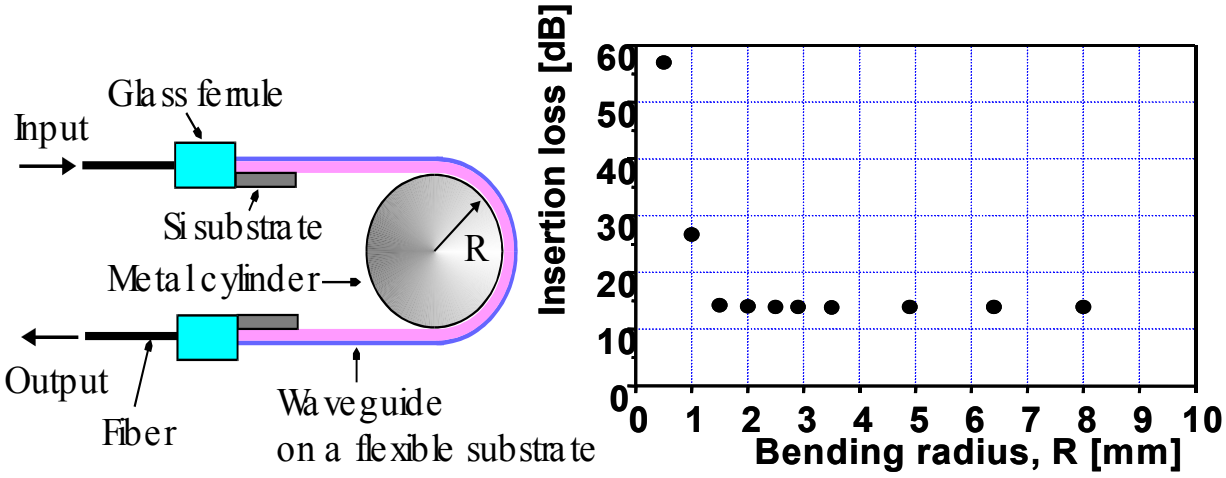


Figure 6. A test bed for measuring optical loss as a function of bending organic electro-optic modulators is shown (left) and typical measurements are shown on the right.

Note that no change in waveguide loss is observed until a bending radius of 1.5 mm is reached. This is clearly an amazing result (but is consistent with are detailed analysis of optical loss in ring microresonator structures (reference 9 and unpublished data). The same observation holds for drive voltage and bias voltage.

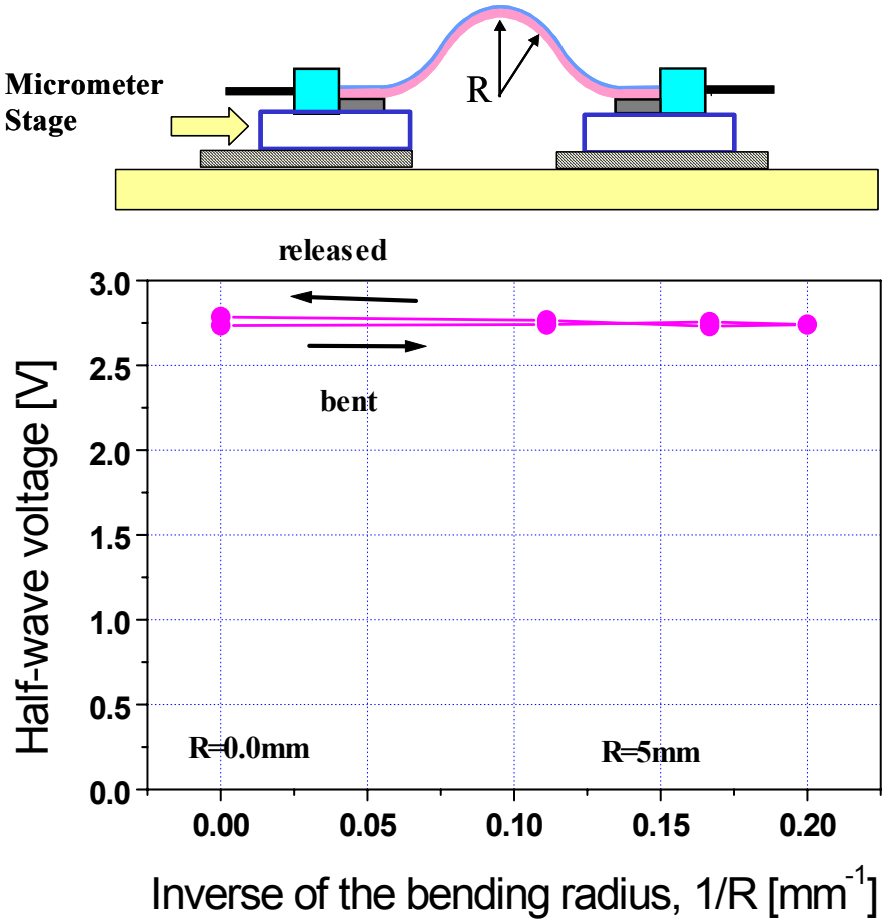


Figure 7. A second test bed for measuring the performance of organic electro-optic modulators with bending is shown (top) and typical results are shown on the bottom. Within experimental error, no change in drive (halfwave or V_π) voltage is observed upon repeated bending.

The results shown in Figs. 6 and 7 illustrate a unique advantage of organic electro-optic materials relative to crystalline inorganic materials such as lithium niobate; namely, that they are conformal and flexible. These properties can be critical to applications such as conformal and space deployable phased array radar antenna.

The enormous potential for technological and societal impact of the proposed research is evident. Our electro-optic and sensor paint materials are already being commercialized both by major corporations (such Boeing) and by start-up companies (such Lumera). Our OLED materials are already of interest to several companies including DuPont. Given that the proposed research should yield dramatic improvement in both performance these materials and transition photovoltaic and organic semiconductor materials to improved performance through realization of improved charge mobilities, etc., it is clear that the technological impact could be significant.

We believe that our research will also have a significant impact on both undergraduate and graduate education (and perhaps even upon 10^{th} –12^{th} grade high school students). Let us cite some examples. We interacted with (mentored) Mr. Field Cady while he was a high school student at Klahowya High School on the Kitsap Pennisula (WA). Currently, Mr. Cady is a Freshman majoring in science at Stanford University (supported by a Stanford scholarship). Mr.

Cady will be working as a summer undergraduate research assistant in our laboratory in the summer of 2004. He was one of 7 high school students from King and Kitsap Counties that I mentored last year (and continue to mentor), an activity that has clearly promoted interest in science in particular and scholastic performance in general on the part of the students. We believe that our research program has provided exceptional training for both undergraduate and graduate students. Evidence in support of this statement is the number of awards won by these students. The research and education experience provided by our laboratories affords the advantage of a clear demonstration of fundamental scientific principals including the role of electrostatic interactions in defining chemical and physical states of matter and a clear demonstration of the advantage of an interdisciplinary approach to science. I lecture in Nanotechnology Ph.D. program courses at the University of Washington and am one of the founders of the Center for Technology Entrepreneurship (which facilitates interaction of Science, Engineering, Business, and Law students). My graduate students have pursued interactions ranging from NSF Education Division programs focused on K-12 to CTE venture laboratory experiments focused on analyzing the process of technology transfer. I also serve on the Advisory Board of the Center for Research and Education on Advanced Materials at Norfolk State University (a HBCU). This has facilitated the recruitment of at least one Afro-American student to our laboratory for a summer research experience over the past several years. Thus, my laboratory presents a diverse array of individuals and professional interests that provides a broad educational experience to those present.

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